DIRECT POLYETHYLENE FINGERPRINTING BY PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (PY-CSIA)

N.T. Jiménez-Morillo [a], F.J. González-Vila [a], G. Almendros [b] and J.A. González-Pérez [a]

(a) Institute for Natural Resources and Agrobiology of Seville (IRNAS, CSIC), Avda. Reina Mercedes, 10. Sevilla, 41012 (Spain).
(b) Centro de Ciencias Medioambientales, CSIC, Serrano 115B, 28006-Madrid, Spain.

Introduction

Polyolefins or polyalkenes are a class of polymers extensively used in the industry because of its characteristics that depend on the arrangement of their ethylenes in crystalline form (high density polyolefin "HDPE") or amorphous (low density polyolefin "LDPE").

New analytical pyrolysis hyphenized techniques can provide valuable information (processes, origin and fingerprinting) about natural and synthetic polymers. In this communication the chemical structure of a low-density green polyethylene and a high-density white polyethylene were studied in detail using conventional micro-furnace analytical pyrolysis, bulk stable isotopic analysis and pyrolysis released compound specific stable isotopic analysis.

Methods

Pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) was performed for polymer characterization using a double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to a GC/MS system Agilent 6890N. Compound assignment was achieved via single-ion monitoring for various homologous series, via low-resolution mass spectrometry, and comparison with published and stored (NIST and Wiley libraries) data. Bulk isotopic signature of light elements ($\delta^{15}N$, $\delta^{13}C$, $\delta^{18}O$ and δD) was analyzed using a Flash 2000 HT (N, C, S, H and O) elemental analyzer (EA/TC) coupled to a Delta V Advantage IRMS (Thermo Scientific) (IRMS).

Compound specific isotope analysis (CSIA) of stable light elements C, N, and H was measured directly in the pyrolysis products from the plastic (Py-GC- (FID)-C/TC-IRMS). This was done by coupling a pyrolysis unit (double-shot pyrolyzer (Frontier Laboratories, model 3030D) – to a gas chromatograph fitted with a flame ionization detector (GC/FID) and coupled to the Delta V Advantage IRMS through a GC-Isolink System (Thermo Scientific) capable of both combustion (C) and high temperature/pyrolysys (TC) (Py-GC-(FID)-C\TC-IRMS). Isotopic ratios are reported as parts per thousand (‰) deviations from appropriate standards recognized by the international atomic energy agency (IAEA).

Figure 1. Low density polyolefin (LDPE) with a green dye

Figure 2. High density polyolefin (HDPE) without a dye

Figure 3. Partial view of the IRNAS Stable isotopes laboratory with main instruments

Results and Discussion

Analitical pyrolysis (Py-GC/MS): a series of *n*-alkane, α-alkene and α,ω-diene (C8 to C37 chain length) were released in each poliolefine (white and green). A peak at *c.* min. 6 was identified as *o*-Chloroaniline (1- Amino-2-chlorobenzene) corresponding to the plastic's green dye (fig. 4C).

Bulk isotopic analysis (TC/EA-IRMS): The values obtained for the whole white polymer were δD=-102.1±0.4 ‰, $\delta^{18}O$ was not detected due to there was not any compound with oxygen. The value of whole green polymer were $\delta^{13}C$=-30.2±0.6 ‰, δD=-79.2±0.3 ‰ and $\delta^{18}O$= +15.3±0.6 ‰; $\delta^{15}N$ was not detected due to a relative low signal contribution from the sole N bearing compound.

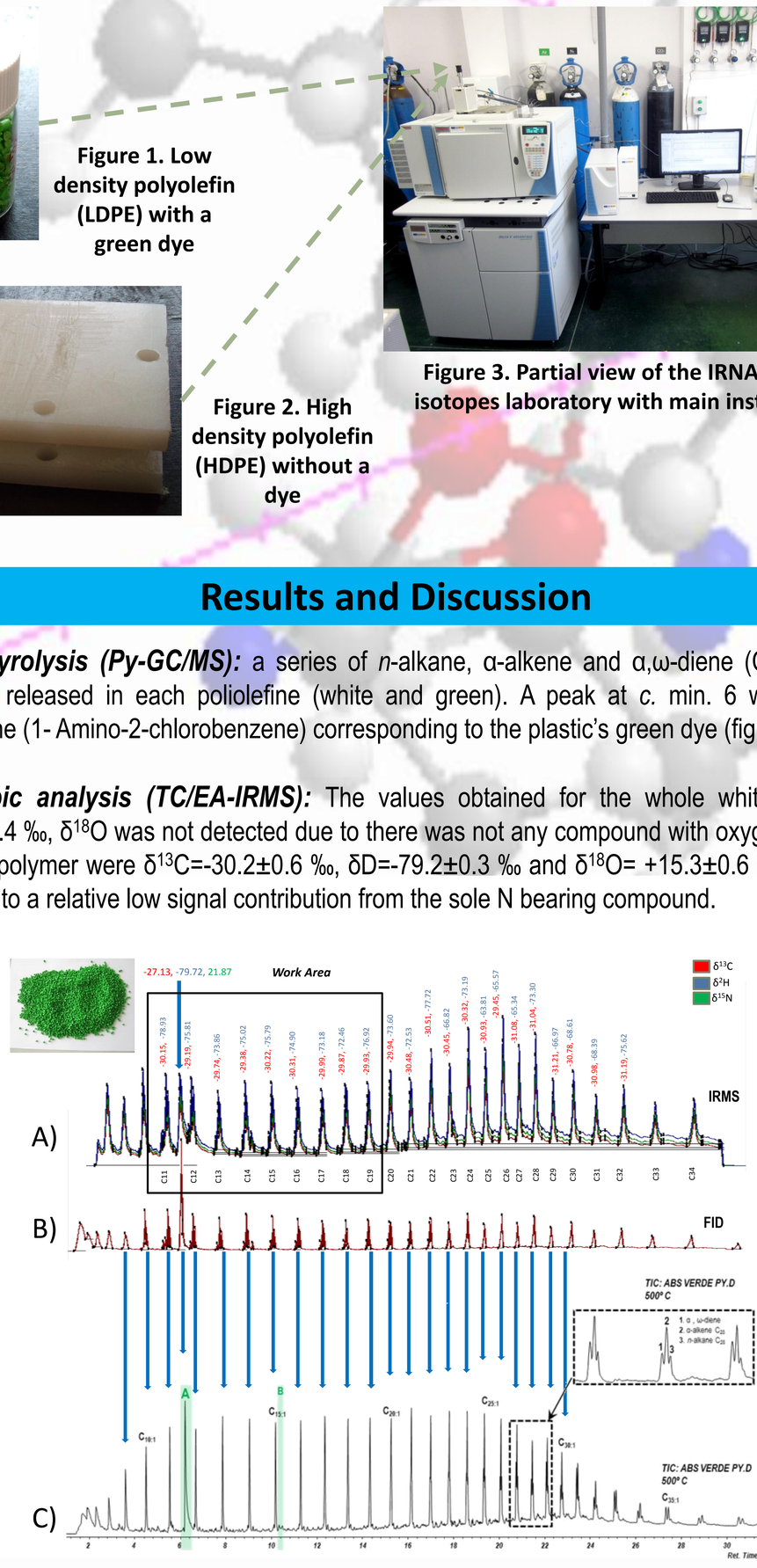

Figure 4 . A) Carbon (C-IRMS) pyrogram; B) FID pyrogram and C) MS total ion current pyrogram (TIC) of a green plastic

Compound specific isotopic analysis (Py-GC-(FID)-C/TC-IRMS): For the green polyethylene plastic, the carbon isotopic signature was similar $\delta^{13}C$ (-30.1±0.6 ‰) for the three homologous series resolved (α,ω-diene -29.5±0.7 ‰; α-alkene -29.9±0.4 ‰; *n*-alkane -30.3±0.5 ‰) but different from that of the green dye (o-Choloroaniline) (-27.1±0.6 ‰). This was the only N bearing structure and $\delta^{15}N$ was obtained (+21.9±2.0 ‰). These signatures are in line with tabulated values for synthetic materials but also indicate that polyolefin and dye are probably from a distinct origin (Fig. 4A). No C data is available for the white polymer.

In the range where it was possible to unambiguously measure isotope ratio (Work area: no-coelution zone between C12 and C19), significant differences were observed in the average compound specific δD values for the three structures for each polyethylene sample; Low-density polymer: α,ω-diene -67.4±3.0 ‰; α-alkene -74.7±1.5 ‰; *n*-alkane -98.9±5.4 ‰; High-density polymer: α,ω-diene -106.2±3.3 ‰; α-alkene -100.9±5.3 ‰; *n*-alkane -115.3±3.2 ‰.

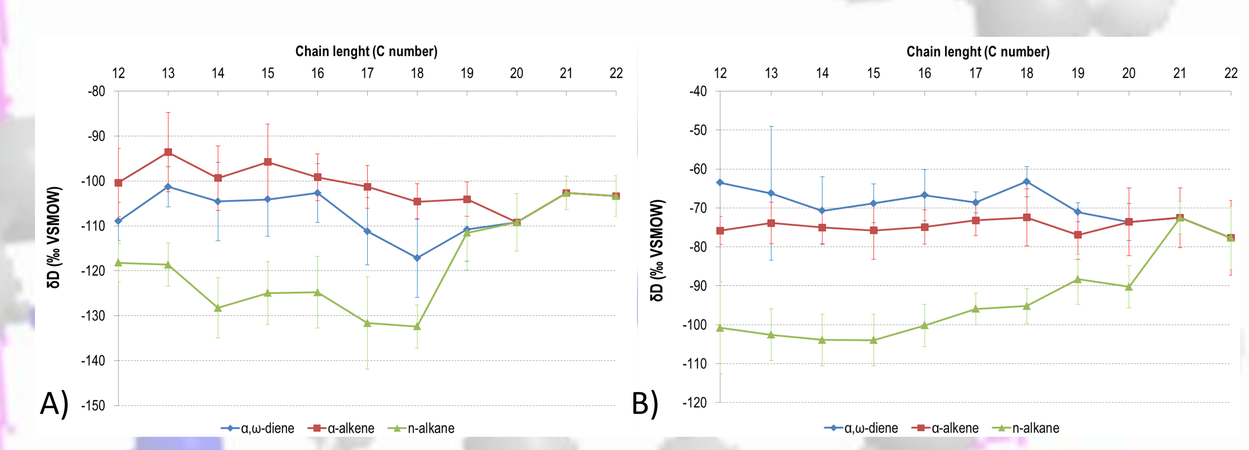

Figure 5. Variation of δD value with carbon number in unsaturated (α,ω-diene, α-alkene) and saturated (*n*-alkane) compounds for HDPE (A) and LDPE (B) samples.

Figure 5 shows Py-CSIA δD values obtained for the three hydrocarbon structures in each polymer samples. For the three hydrocarbon structures LDPE plastic have higher δD vales than HDPE, this may be explained using two hypotheses: a) δD value reflects differences in feedstock origin used in the fabrication of each plastic, or b) the δD differences depends on the plastic's chemical structure, HDPE has a linear structure with a few branching and tertiary carbon atoms whereas the LDPE plastic presents a spherical structure with many branching and a high number of tertiary carbon atoms.

Figure 6 illustrates a theoretical model to explain the differences observed between the three hydrocarbon structures produced by pyrolysis of a low density plastic (LDPE). Tertiary carbon atoms in the plastic net (red balls) may act as deuterium (blue balls) concentrators due to its higher polarity than that of primary or secondary carbons. In fact, double bond resonance from a carbanion (C-) produced by the scissions in tertiary C may behaves as a concentrator of the heavy (D) hydrogen isotope (Fig. 7). In the case of the HDPE sample the chemical structure is similar to LDPE but linear, with no branching present.

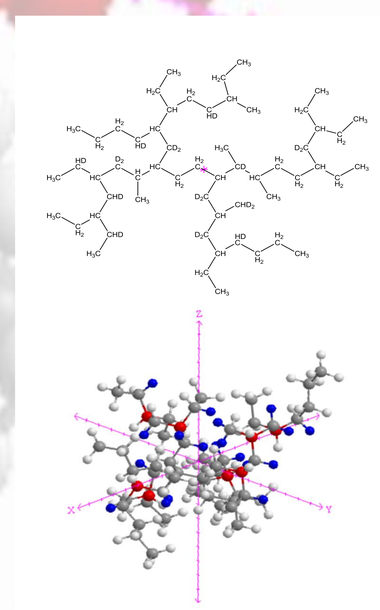

Figure 6 . Theoretical model of la low-density polyolefin (LDPE). Deuterons (blue), hydrogens (white), carbons (gray) and tertiary carbons (red).

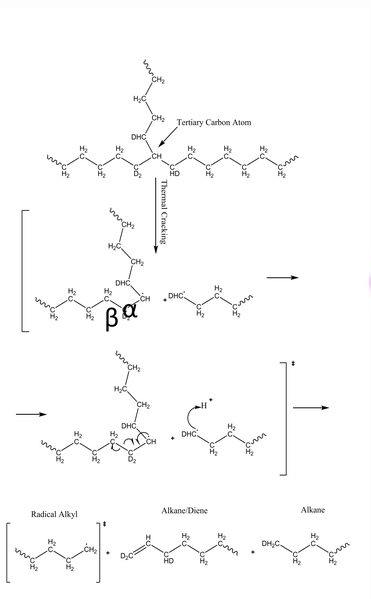

Figure 7. Theoretical model of thermal cracking and formation of *n*-alkane, α-alkene and α, ω-diene, by breaking the β carbon.

Significant differences were found in δD values between saturated and unsaturated chains, but no between the unsaturated (α,ω-diene, α-alkene) moieties (Fig 5). In both plastic types, the observed tendency of *n*-alkane enrichment in deuterium with chain length, could be explained as a dual effect or a combination of: a) dilution effect with increasing chain length and b) a peak coelution effect.

The described δD hydrocarbon enrichment with chain unsaturation is being further investigated and has to be taken into consideration when measuring compound specific δD in polymeric materials using hyphenated Py-CSIA. This is a powerful and fast tool to characterize polymeric materials like polyolefins or other synthetic plastics as well as to detect additives and its potential uses in the plastic industry are being explored.

Acknowledgments

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